



# Investigation of thermal aging and hydrolysis mechanisms in commercial lithium ion battery electrolyte



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## HIGHLIGHTS

- Investigations on the thermal stability of LiPF<sub>6</sub> in presence of water.
- Investigations and identification of decomposition products with a new method in an LIB electrolyte.
- Proposed reaction cycle for the electrolyte system.

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## ABSTRACT

Novel methods based on hyphenated analytical techniques for the analysis of LiPF<sub>6</sub> commercially available battery electrolytes are presented. PF<sub>6</sub><sup>−</sup> and the formed main decomposition products F<sup>−</sup>, PO<sub>2</sub>F<sub>2</sub><sup>−</sup> and HPO<sub>3</sub>F<sup>−</sup> were separated by ion chromatography (IC) and detected by electrospray ionization mass spectrometry (ESI-MS). Inductively coupled plasma optical emission spectroscopy (ICP-OES) on the phosphorous trace supported the results obtained by ESI-MS. Samples, which were stored at room temperature and at 5 °C, were analyzed several times over a period of two weeks to demonstrate the progress of the hydrolysis of LiPF<sub>6</sub> in aqueous solution and commercially available electrolyte (EC/DEC (3:7 w/w) 1 M LiPF<sub>6</sub>). Subsequently, the same commercially available electrolyte system was analyzed to prove the usefulness of the proposed method to investigate the influence of the thermal aging in lithium-ion batteries.

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## 1. Introduction

Lithium ion batteries (LIBs) are one of the most important energy sources for portable electronic devices, e.g. mobile phones or notebooks [1,2]. However, when packed in large batteries, such as those required for EV and HEV applications, LIBs are prone to accelerated aging and low safeness. The electrolytes of conventional LIBs typically consist of a mixture of linear and cyclic organic carbonates and lithium hexafluorophosphate (LiPF<sub>6</sub>) as electrolyte salt due to its high conductivity, SEI forming ability and aluminum (cathode current collector) protection. However, using LiPF<sub>6</sub> is disadvantageous due to its thermal instability as observed by differential scanning calorimetry (DSC) and adiabatic calorimetry

(ARC) [3,4]. Additionally, due to the high hygroscopicity of LiPF<sub>6</sub>, battery grade electrolytes contain about 25 ppm water [5,6], which favors spontaneous decomposition reactions since LiPF<sub>6</sub> is decomposed in the presence of water [7].

In literature the following steps for the hydrolysis of LiPF<sub>6</sub> are reported to take place [8–11]:



Besides its dissociation to Li<sup>+</sup> and PF<sub>6</sub><sup>−</sup>, LiPF<sub>6</sub> is also in equilibrium with lithium fluoride (LiF) and phosphorus pentafluoride

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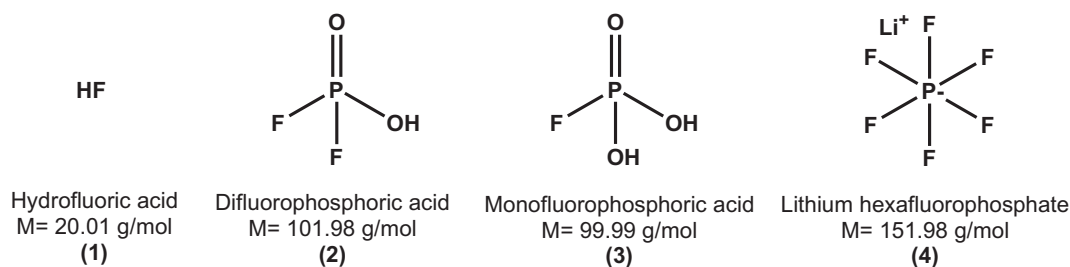
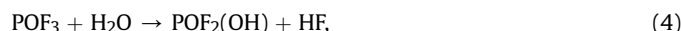


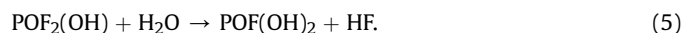
Fig. 1. Structural formula and molecular weight of  $\text{LiPF}_6$  and the hydrolysis decomposition products.

( $\text{PF}_5$ ) in aqueous solution. By interaction between the strong Lewis acid  $\text{PF}_5$  and water, phosphorus oxyfluoride ( $\text{POF}_3$ ) is formed [12].

Plakhotnyk et al. already studied the decomposition of  $\text{LiPF}_6$  in the water containing propylene carbonate–dimethyl carbonate system by  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectroscopy [13]. They suggested that  $\text{POF}_3$  further decomposes in presence of water to difluorophosphoric acid ( $\text{POF}_2(\text{OH})$ ),



which is followed by the reaction between the formed  $\text{POF}_2(\text{OH})$  and water under formation of monofluorophosphoric acid ( $\text{POF}(\text{OH})_2$ ):



The proposed decomposition products including structural formula and molecular weight are depicted in Fig. 1.

In a previous work [22] it was shown the usefulness of ion chromatography to investigate the decomposition products of  $\text{LiPF}_6$ . As a further step towards the understanding of aging phenomena in LIBs, the ion chromatography (IC) method presented in this work was developed to separate the decomposition products of  $\text{LiPF}_6$  and other compounds formed during the thermal aging of a commercially available electrolyte system EC/DEC (3:7 w/w). However, in this work UV–vis detection was replaced with conductivity detection and for unknown compounds, electrospray ionization mass spectrometry (ESI-MS) and inductively coupled plasma optical emission spectroscopy (ICP-OES) were complementary used for detection and identification purposes.

## 2. Experimental

### 2.1. Chemicals

Anhydrous sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), sodium bicarbonate ( $\text{NaHCO}_3$ ) and battery electrolyte were purchased from Merck KGaA (Darmstadt, Germany). Acetonitrile (AcN, HPLC grade) was obtained from VWR International GmbH (Darmstadt, Germany). Battery grade lithium hexafluorophosphate was ordered from

Sigma–Aldrich Chemie GmbH (Steinheim, Germany). All chemicals were of the highest quality available. Purified water ( $18.2 \text{ M}\Omega^{-1} \text{ cm}^{-1}$ , TOC <4 ppb, Milli-Q Advantage A10, Millipore GmbH, Schwalbach, Germany) was used for all experiments.

### 2.2. Instrumentation

A Basic IC 792 ion chromatograph and an 881 Compact IC pro Anion MCS from Metrohm AG (Herisau, Switzerland) were used for IC measurements. Both systems consisted of a suppressor for chemical suppression, which acts as a cation exchanger to remove cations and replace them with an  $\text{H}^+$  so that the background noise is lowered to  $1 \mu\text{S}$  and a conductivity detector.

For IC/ESI-MS measurements, an API2000 and a QTRAP3200 mass spectrometer from Applied Biosystems (Darmstadt, Germany) were used with an electrospray ionization source.

For IC/ICP-OES measurements, a SPECTRO ARCOS from SPECTRO Analytical Instruments GmbH (Kleve, Germany) was used with a cyclone spray chamber and a MiraMist Teflon® nebulizer (Burgener, Mississauga, Ontario, Canada).

The software used for controlling the IC was the 792 Basic IC 1.0 (Metrohm). The API2000 and QTRAP3200 were controlled by the Analyst 1.4.1 and 1.5.1 softwares respectively, (both from Applied Biosystems). The SPECTRO ARCOS was controlled by the Smart Analyzer Vision 4.0 software (SPECTRO).

### 2.3. Analytical procedures

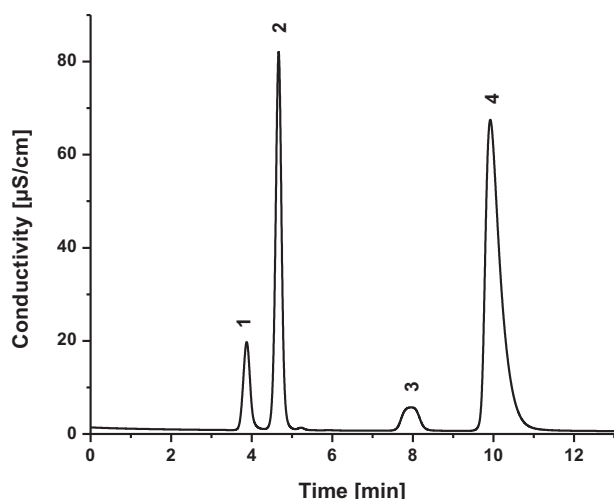
A solution of  $\text{LiPF}_6$  in water ( $10 \text{ mmol L}^{-1}$ ) was analyzed by IC with conductivity detection. For the hyphenation of IC with ICP-OES or ESI-MS a solution of  $1 \text{ mmol L}^{-1}$   $\text{LiPF}_6$  in water was prepared, which was stored at room temperature. Based on Karl Fischer measurements, the electrolyte contained 25 ppm of water. A commercially available battery electrolyte containing  $1 \text{ mol L}^{-1}$   $\text{LiPF}_6$  with EC/DEC (3:7 w/w) was spiked with 600 ppm ( $3.3 \cdot 10^{-2} \text{ mol L}^{-1}$ ) of purified water. Afterwards the electrolyte was stored at room temperature. A non-spiked electrolyte sample was stored at  $35^\circ\text{C}$  for the thermal aging investigations to show the different impact of temperature in contrast to water content.

Table 1  
ICP-OES operation conditions for IC/ICP-OES analyses.

Parameter	ICP-OES value
Injector tube	2.5 mm
Nebulizer gas flow	$0.5 \text{ L min}^{-1}$
Auxiliary gas flow	$2.0 \text{ L min}^{-1}$
Cooling gas flow	$12.0 \text{ L min}^{-1}$
RF power	1400 W
Integration time	500 ms
Run time	15 min

Table 2  
ESI-MS parameters for IC/ESI-MS analyses.

Parameter	ESI/MS value
Nebulizer gas	90 psi
Dry gas	90 psi
Temperature	$400^\circ\text{C}$
Ion spray voltage	$-4200 \text{ V}$
Declustering potential	$-60 \text{ V}$
Focusing potential	$-200 \text{ V}$
Entrance potential	$-10 \text{ V}$



**Fig. 2.** Chromatogram of lithium hexafluorophosphate (aqueous solution) with conductivity detection. Four peaks were detected: **1** 3.45 min, **2** 4.25 min, **3** 7.37 min and **4** 10.86 min. Peak **1** was identified as  $F^-$  by standard.

#### 2.4. IC conditions

Separation of the hydrolysis products of  $LiPF_6$  was carried out using an anion separation column model Metrosep Supp 4 (Metrohm, Herisau, Switzerland) with the following dimensions: 250 mm length  $\times$  4.0 mm i.d., 9  $\mu$ m particle size. A Metrosep Supp 4/5 guard (Metrohm) was used to avoid contamination of the analytical column. The flow rate of the mobile phase was 0.9 mL  $min^{-1}$ . For isocratic separations, the mobile phase consisted of a solution of 2.0 mmol  $L^{-1}$  sodium bicarbonate and 4.2 mmol  $L^{-1}$  sodium carbonate in a mixture of 30% acetonitrile (AcN) and 70% water (v/v). The injection volume was 20  $\mu$ L.

#### 2.5. Hyphenation and ICP-OES conditions

The IC system was coupled to the ICP-OES using PEEK tubing with an inner diameter (i.d.) of 0.25 mm. The PEEK tubing was directly connected to a MiraMist Teflon<sup>®</sup> nebulizer (Burgener, Mississauga, Ontario, Canada) and a cyclonic spray chamber, which was operated at room temperature. ICP-OES parameters are presented in Table 1.

#### 2.6. ESI-MS conditions

For IC/ESI-MS analysis, the IC system was directly connected to the ionization interface using PEEK tubing with an i.d. of 0.25 mm. The eluting analytes were ionized in the ESI interface in the negative ion mode. ESI-MS parameters are presented in Table 2.

### 3. Results and discussion

#### 3.1. Analysis of $LiPF_6$ by IC

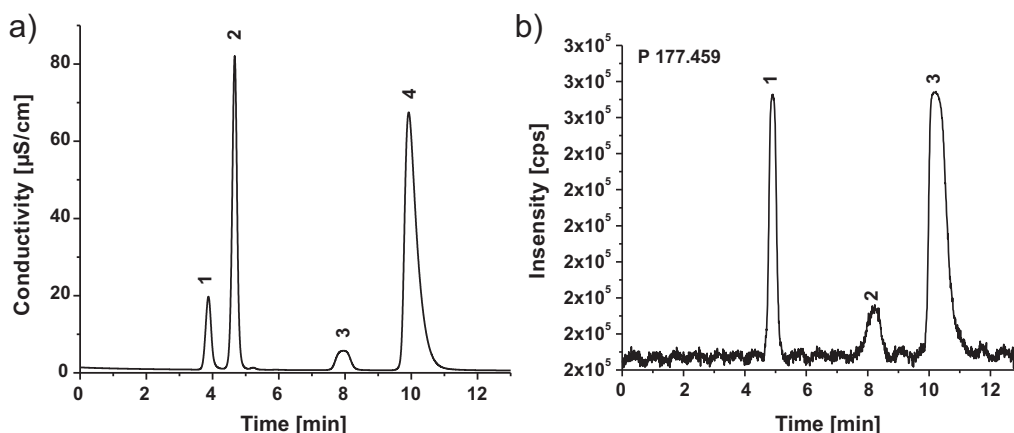
Qualitative analysis of  $LiPF_6$  based on IC with a conductivity detector, IC/ESI-MS and IC/ICP-OES was carried out to identify its decomposition products in aqueous solution. A lithium hexafluorophosphate sample (aqueous solution), which was stored for four weeks was analyzed by IC. In Fig. 2, the chromatogram of the sample with conductivity detection is presented. Four peaks were detected with the following retention time: **1** 3.45 min, **2** 4.25 min, **3** 7.37 min and **4** 10.86 min. Baseline separation was obtained for all of the decomposition products. By comparison with a standard, peak **1** was identified as fluoride.

Further peaks in the chromatogram could not be identified by IC using conductivity detection. However, considering the hydrolysis rate, which is described in literature as slow, peak **4** could belong to hexafluorophosphate [14,15]. Furthermore, studies have shown that difluorophosphate ( $F_2PO_2^-$ ) can be formed by the hydrolysis reaction [16–19]. According to these studies and the proposed hydrolysis reaction scheme, it is expected that the peaks might consist of difluorophosphoric acid and monofluorophosphoric acid.

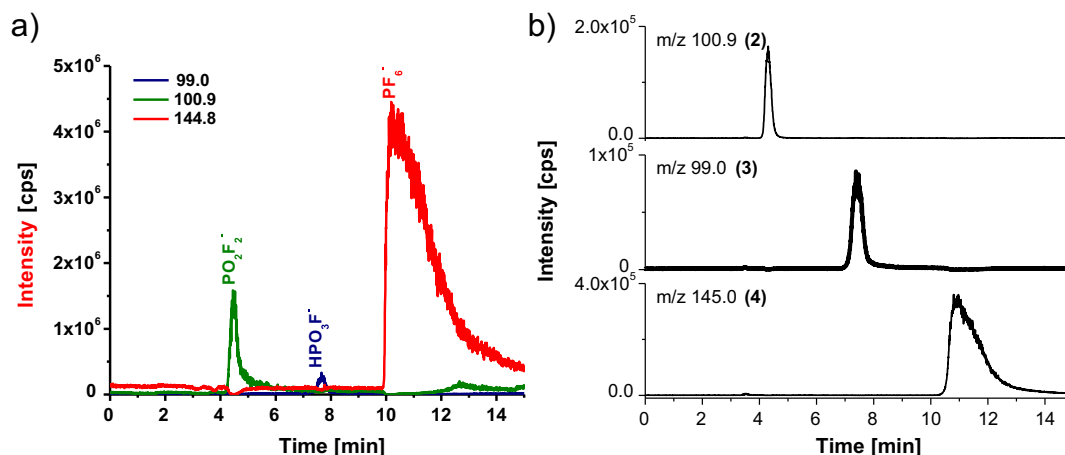
Complementary analyses for identification purposes were therefore performed by IC/ICP-OES and IC/ESI-MS, which results are presented in the following.

#### 3.2. IC/ICP-OES detection

To get some information about the element composition of each peak the IC was coupled with the ICP-OES. The conductivity detector was also used for comparison. Fig. 3a shows the chromatogram with conductivity detection of the above-mentioned  $LiPF_6$  aqueous solution stored for four weeks at room temperature. In Fig. 3b, the chromatogram of the  $LiPF_6$  sample with ICP-OES detection at the phosphorous trace is shown. Three baseline-separated peaks (peaks **2**, **3** and **4**) were detected. Compared with Fig. 3a, the peaks hold the same retention times. Hence, peaks **2**, **3** and **4** are phosphorus compounds.



**Fig. 3.** (a) Conductivity chromatogram of hydrolyzed lithium hexafluorophosphate stored for four weeks at RT: **1**  $F^-$ , **2–4** further decomposition products. (b) Chromatogram of the IC/ICP-OES analysis of a hydrolyzed lithium hexafluorophosphate sample stored for six weeks at RT: peaks **2–4** are containing phosphorus. The phosphorus emission was detected at 177.459 nm.



**Fig. 4.** (a) ESI-MS mass spectra of the investigated hydrolyzed lithium hexafluorophosphate. The sample was stored for four weeks at room temperature: **1**  $\text{F}^-$ . (b) Single ion mode (SIM) chromatogram of the IC/ESI-MS analysis of a hydrolyzed lithium hexafluorophosphate sample stored for four weeks at RT:  $m/z$  100.9 **2**  $\text{PO}_2\text{F}_2^-$ ,  $m/z$  99.0 **3**  $\text{HPO}_3\text{F}^-$  and  $m/z$  145.0 **4**  $\text{PF}_6^-$ .

### 3.3. IC/ESI-MS detection

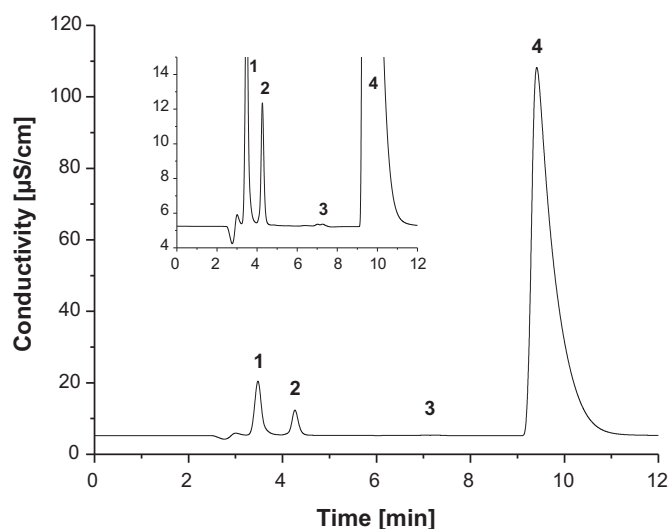
For identification of the detected decomposition products, the IC was connected to ESI-MS. The compounds were analyzed first with conductivity and afterwards with ESI-MS detection. In Fig. 4a the ESI-MS chromatogram of the aqueous  $\text{LiPF}_6$  sample is shown. The sample was stored four weeks at room temperature. The chromatogram reveals three peaks, since  $\text{F}^-$  cannot be analyzed by this mode, but was already identified earlier. The corresponding chromatograms recorded with ESI-MS in single ion mode (SIM) are presented in Fig. 4b. The decomposition products were identified by their  $m/z$  ratio. Difluorophosphoric acid **2** was detected with  $m/z$  100.9 at  $t_R = 4.25$  min, monofluorophosphoric acid **3** with  $m/z = 99.0$  at  $t_R = 7.36$  min and hexafluorophosphate **4** with  $m/z = 145.0$  at  $t_R = 11.01$  min.

### 3.4. Analysis of a commercially available battery electrolyte

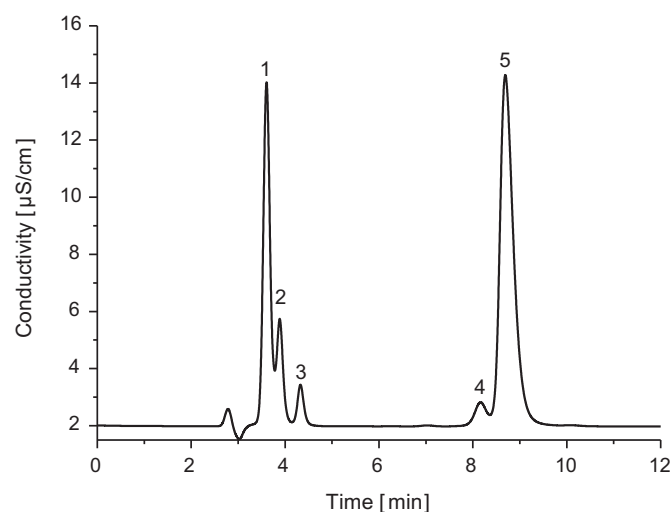
In Fig. 5, the chromatogram (conductivity detection) of a commercially available battery electrolyte containing  $\text{LiPF}_6$  is

presented. The sample was spiked with 600 ppm of water and stored at room temperature for several weeks. While peak **1** was identified as fluoride (see Section 3.1),  $\text{PF}_6^-$  (**4**), difluorophosphate (**2**) and monofluorophosphate (**3**) were detected as well. Comparing the chromatograms of  $\text{LiPF}_6$  in water (Fig. 2) or electrolyte (Fig. 5), it appears as in the latter the area of monofluorophosphate is almost negligible. Furthermore, the relative peak areas of fluoride and difluorophosphate in the electrolyte solution are relatively small compared with that of hexafluorophosphate, which is the far most intense peak in Fig. 5. This results support for very different decomposition rates resulting from the lower dielectric constant of the electrolyte [20]. While  $\text{LiPF}_6$  completely dissociates in water, ion pairs often occur in organic solvents, which in turn changes the reaction path [21]. In this case, the decomposition rate of  $\text{LiPF}_6$  decreases, which entails less electrolyte degradation in the cell.

In Fig. 6, the chromatogram of the commercially available electrolyte (without water addition) stored at 35 °C for the same time (4 weeks) is shown. Here, several new decomposition products appear due to the temperature influence on the system. Notice that in order to avoid peak overlapping the sample was additionally



**Fig. 5.** Chromatogram (conductivity detection) of commercially available battery electrolyte spiked with 600 ppm of water.



**Fig. 6.** Chromatogram (conductivity detection) of commercially available battery electrolyte aged at 35 °C.

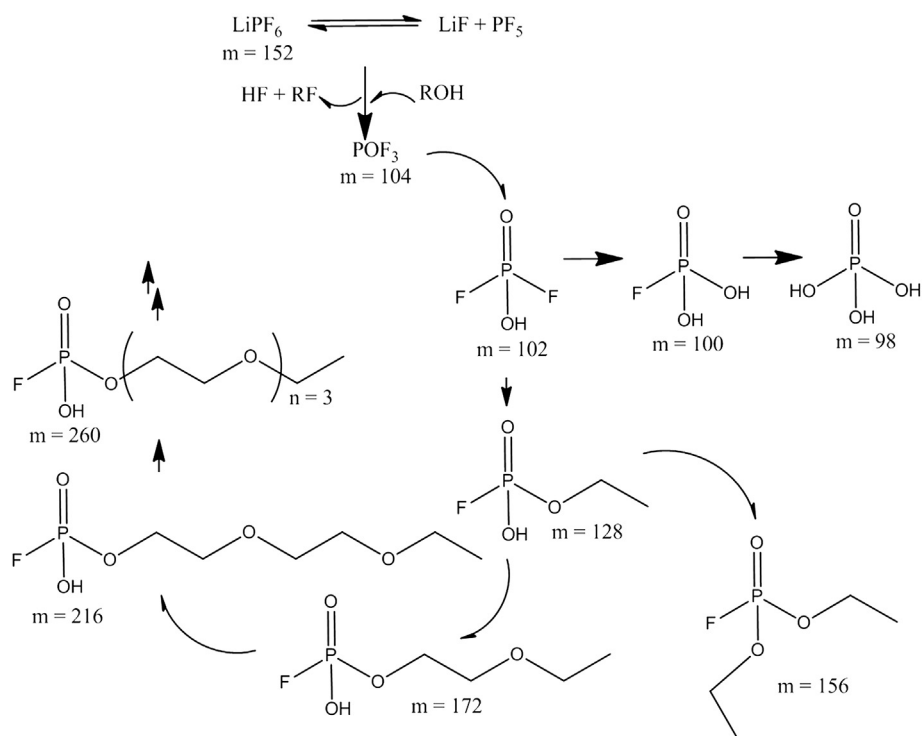


Fig. 7. Preliminary reaction cycle for the decomposition process of the electrolyte system EC/DEC (3:7 w/w) and 1 M LiPF<sub>6</sub>.

tenfold diluted. IC/ESI-MS was used to identify the compounds separated by IC, as described earlier. All the compounds which were found in the water spiked sample were also present in this chromatogram: (1), fluoride, (3), difluorophosphate (5), PF<sub>6</sub><sup>-</sup> and (2) monofluorophosphate. Additionally peak (2) revealed a contribution from FPO<sub>3</sub>C<sub>2</sub>H<sub>5</sub> while peak (4) was generated by the following decomposition products FPO<sub>4</sub>C<sub>4</sub>H<sub>10</sub>, FPO<sub>5</sub>C<sub>6</sub>H<sub>14</sub> and FPO<sub>6</sub>C<sub>8</sub>H<sub>18</sub>, which were all detected as single charged anions. It is interesting to point out that the influence of temperature had a more important impact on the decomposition process than the spiked water, although only a minor increase from 25 °C to 35 °C was investigated. This indicates that only a small amount of water is needed to start the decomposition processes, which kinetics are, on the other hand, highly increased by temperature. Since the carbonates release CO<sub>2</sub> during the aging process, the resulting alcohols act as an additional reaction source.

Additionally, the relatively low amount of water present in the commercial electrolyte (up to 25 ppm) is certainly not enough for reactions (3)–(5) (see above) to proceed since water is stoichiometrically involved in these reactions. Thus, a totally different mechanism must take place already at 35 °C, which, involving the carbonate solvents, results in the generation of several alkyl- and alkoxy phosphates. Combining the results showed above with GC-MS measurements, which confirmed phosphorus oxyfluoride and diethylfluorophosphate, a preliminary reaction cycle is proposed (Fig. 7) for the electrolyte system regarding thermal aging.

#### 4. Conclusions

A novel method for the analysis of LiPF<sub>6</sub> and battery electrolytes was presented. During the hydrolysis investigations, four degradation peaks were separated by IC and detected with conductivity detection. The separation efficiency of IC allowed baseline separation of all investigated analytes within less than 13 min. Fluoride was identified by standard. Further identifications were carried out

by hyphenation of the IC with both, ICP-OES and ESI-MS. As additional decomposition products difluorophosphate (PO<sub>2</sub>F<sub>2</sub><sup>-</sup>) and monofluorophosphate (HPO<sub>3</sub>F<sup>-</sup>) were identified. Furthermore, it was demonstrated that the determination and identification of decomposition products in commercial battery electrolyte solutions are possible using the newly developed methods.

Additionally, it was shown that temperature influence is more important than water impurities regarding the aging process of the electrolyte. A preliminary reaction cycle was proposed for the thermal decomposition of the investigated system. For future work, a gradient step should be applied instead of the isocratic step, since some of the new compounds, especially those detected at peaks 2 and 4 in Fig. 6, could not be baseline separated. This is important for the quantification of the decomposition products using IC/ICP-OES or IC/ICP-MS since there are no commercially available standards available today.

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